

PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Method for Recovery of Noble Metals

We, TECHNION RESEARCH AND DEVELOPMENT FOUNDATION LIMITED, a body corporate of Israel, of Senate Building, Technion City, Haifa, Israel, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method for the separation of the metals gold, platinum, palladium, and rhodium (herein termed a noble metal) from ore, used catalysts, scrap, residues, or solutions containing these metals (herein termed a noble metal carrier).

More specifically the present invention relates to an ore recovery method characterised by the employment of a chelating agent which constitutes a significant advance over current methods.

Precipitation, cyanidization, amalgamation and electrolysis have been used in the recovery of gold, platinum, palladium and rhodium. Unfortunately, however, these methods have proven to be relatively expensive in terms of energy requirements and are generally considered relatively slow.

Other methods for the recovery of metals such as gold, silver, and nickel from alkaline cyanide solutions make use of weak-base or strong-base anion exchange resin. These anion exchangers have no special affinity for the noble metals gold, platinum, palladium, and rhodium relative to the base metals e.g. zinc, copper, nickel, lead, and iron. Therefore, the anion exchange resin technique does not successfully separate the noble metals when these noble metals are found in combination with base metals. Moreover, the capacity of the anion exchange resins for adsorbing metals is considerably lower than that of the selective chelating resin used in the method of the present invention. Finally, extracting by use of anion exchange resins requires complicated separation processes for the final recovery of

the noble metals. In contradistinction thereto, because of the use of a special chelating agent which does not adsorb base metal, further separations for final recovery are unnecessary.

It is an object of this invention to provide an improved method for the recovery of the noble metals, from ores, used catalysts, metal scrap, residues from chemical processes, spent solutions, and other materials, solutions or suspensions containing or carrying noble metals, particularly when these noble metals occur in combination with one or more of the base metals.

It is another object of this invention to provide a method by which will be obtained the noble metals gold, platinum, palladium, and rhodium in high purity form, with minimal processing.

Yet another object of this invention is to provide a simple, continuous process requiring only gravity circulation or a low energy power source for circulation of solutions containing the noble metals to be extracted.

Accordingly, the invention provides a method for the separation of a noble metal as hereinbefore defined from a noble metal carrier as hereinbefore defined wherein said metal is adsorbed from a solution of the carrier by a selective chelating ion exchange resin comprising a chloromethylated styrene-divinylbenzene resin incorporating thio-urea. Such an ion exchange resin has high capacity and exceptional selectivity for the noble metals, and further separation of the noble and base metals is unnecessary, since the base metals are not adsorbed by the resin.

In the following, one embodiment of the invention is described by way of example with reference to the accompanying drawings in which:—

Figure 1 is a chemical flow diagram;

Figure 2 shows the chemical structure of the selective chelating ion-exchange resin; and

Figure 3 shows an embodiment of one form

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of apparatus which may be employed for the purposes of the present invention.

Referring to the drawings, Figure 1 is a chemical flow diagram showing the extraction of platinum, using the method of this invention, from a solution containing this metal. Before passage through the ion-exchanger the noble metal or metals to be extracted must be dissolved and in solution. The preparation of scrap, residues, used solutions, or used catalysts of the noble metals before extraction is a standard procedure and will not be described here. For the preparation of the solution containing the noble metals to be extracted see "The Rare Metals Handbook" edited by C. A. Hampel, and published by Reinhold Publishing Co., in 1954.

The prepared solution containing the noble metal platinum is passed through an ion exchange column as shown in the first step of Figure 1. Due to the highly selective action of the particular chelating resin used in the method of this invention, and its high capacity for adsorbing noble metals, the platinum is removed from the solution bearing it. The effluent from the ion exchange column is virtually free of platinum, but does contain base metals present in the solution before passage through the ion-exchange column. In the flow diagram of Figure 1, the effluent is shown being discharged after passage through the ion-exchanger. The column containing the special resin is then flushed with a dilute solution of about 0.1 N HCl to remove all traces of base metals present in the solution remaining in the column. Two alternatives are possible for the final recovery of the platinum. The first alternative is to remove the resin from the ion exchanger with its charge of adsorbed platinum, dry this material, and ignite the resin in an oven. As shown in Figure 1 pure platinum will remain as a result of this procedure. If it is desired to have the highly purified platinum in a concentrated solution, then the second alternative as shown in Figure 1 can be utilized. In this alternative, using a standard technique, the column material, i.e., the resin with its adsorbed charge of platinum, is eluted with acid and a complexing agent. The concentrated solution of platinum can be filtered out after elution.

The method of this invention uses a particular chelating ion-exchange resin. The chemical structure of this resin is shown in Figure 2. This material is a Chloromethylated Styrenedivinylbenzene resin in which thiourea has been incorporated. This special resin is prepared as follows:—

Beads of resin are made up from styrene containing 1 to 2% of divinylbenzene in a process of copolymerization. This is a process well known to manufacturers of ion-exchange resins, and fully described in the literature. The beads of resin so produced are then chloromethylated. This process is described by

Pepper, K. W. et al in the J. Chem. Soc., 4097 (1953). The chloromethylated beads of resin are available commercially. Finally, the resin beads are refluxed with thiourea. This process is described by Parrish, J. R., in Chem. & Industry, 137 (1956). It should be noted here that Parrish goes on to hydrolyze the refluxed resin beads. He obtains a redox resin which is not selective for the noble metals.

The above described organic chelating resin has very high capacity for adsorbing noble metals. Laboratory tests to determine the maximum capacity of adsorption of the resin has yielded the following results:—

For gold, the maximum adsorptive capacity was found to be 0.85 grams of gold per gram of resin; for platinum, the maximum adsorptive capacity was found to be 0.50 grams of platinum per gram of resin; and, for palladium, the maximum adsorptive capacity was found to be 0.30 grams of palladium per gram of resin. Quantitative results for the noble metal rhodium have not yet been completed, but the organic resin of the method of this invention has been found to be highly selective for this noble metal also.

Figure 3 shows, by way of example only, the simple apparatus used according to the method of this invention. A vessel holding the solution, 1, containing platinum and/or other noble metals in addition to any combination of base metals, is connected so that this solution can flow by gravity to the ion exchange column container 2. The column container is packed with beads 3, of size about 20 to 50 mesh (B.S.S.), of chloromethylated styrenedivinylbenzene resin in which thiourea has been incorporated. Adjacent to the output of the ion exchange column, is a filter plug 4, to prevent particles of the resin from flowing out of the column with the effluent 6. To control the flow of solution through the ion exchange column, the stop cock 5, is used. Once the solution has passed through the column and the column material is flushed with dilute hydrochloric acid, the column resin, with its charge of adsorbed noble metal, is removed by withdrawing the stopper 7. The column material is then either roasted to obtain noble metal(s) in pure metallic form, or it can be eluted with an acid and complexing agent to obtain a concentrated solution of the noble metal(s), free of any base metals.

The effectiveness of the present invention is amply demonstrated by the following working examples:—

EXAMPLE I

Powdered ore from Northern Ontario sources known to contain approximately 200 to 400 micrograms of the subject noble metals per 30 grams of ore was diluted in aqua regia and filtered to remove insolubles. The filtrate was then evaporated in order to eliminate nitric oxides and to reduce acidity and diluted with

water to further reduce acidity and lower salt concentration. The solution was then passed through a column containing the described resin. Gold, platinum and palladium were adsorbed on the resin. All other constituents of the solution passed freely through the column without being adsorbed.

EXAMPLE II

Thirty grams of copper from the Timna copper mines in Israel was dissolved in aqua regia. Thirty micrograms of gold were added thereto and the sample was filtered to remove insolubles. The filtrate was then evaporated and diluted with water and passed through a column containing the described resin. The subject ore is known not to contain noble metals. Subsequent recovery of the ore was in excess of 90%.

EXAMPLE III

20 litres of a solution containing 1.5 micrograms of gold per litre of water ($7.5 \times 10^{-8}M$) were passed through a column containing 0.200 grams of resin (dimensions of the column were: internal diameter—4 mm, length—66 mm) at the rate of approximately 9.2 l/hr. After the solution had passed through the gold was seen to have accumulated near the top of the column (an intensely yellow strip 5 mm wide appeared at the top end of the column). The resin was then burnt, and photometric analysis showed that the entire 30 micrograms of gold had been adsorbed on the resin. This fact points to the possibility of binding gold from even more dilute solution to the column. A further possibility is an increase in the rate of flow, if a longer column is used.

The same procedure may be adopted with respect to platinum and palladium.

For treating spent catalysts, the following procedure has been found most effective: First the catalyst is rinsed in water, filtered, and the solid residue dissolved in aqua regia. The solution is then filtered to remove separate solids and the filtrate evaporated to eliminate nitric oxides. Water is then added to reduce acidity and salt concentration and the sample is passed through a column containing the subject resin.

Sludge is treated in a manner similar to

that used on ores; thus the sludge is dissolved in aqua regia, evaporated, diluted with water and passed through a column.

The resin beads may be made as follows, using the commercially available copolymer styrene linked with divinyl benzene.

50 grams of this copolymer are immersed in 200 millilitres of chloromethyl methyl ether for 2 hours. Then an additional 100 millilitres of the ether are added, together with 15 millilitres of anhydrous stannic chloride, the mixture being refluxed for 1 hour. After cooling, the beads are separated by filtration, thoroughly washed with dioxane and ethyl alcohol, and dried.

50 grams of the resulting chloromethylated beads are immersed overnight in dioxane for swelling. When the swelling is completed, 30 grams of thio-urea dissolved in 100 millilitres of water are added, and the whole is refluxed for 1 hour. Finally, the product is separated, thoroughly washed with water, and dried.

WHAT WE CLAIM IS:—

1. A method for the separation of a noble metal as hereinbefore defined from a noble metal carrier as hereinbefore defined wherein said metal is adsorbed from a solution of the carrier by a selective chelating ion exchange resin comprising a chloromethylated styrene-divinyl-benzene resin incorporating thio-urea.

2. A method according to claim 1 wherein the noble metal is recovered by roasting the resin and adsorbed noble metal to burn off said resin.

3. A method according to claim 1 wherein the solution of the carrier is passed through the resin.

4. A method according to any one of the preceding claims wherein the chelating ion exchange resin has the empirical formula shown in Figure 2 of the accompanying drawings.

5. A method according to any one of the preceding claims substantially as described with reference to any one of the Examples I—III.

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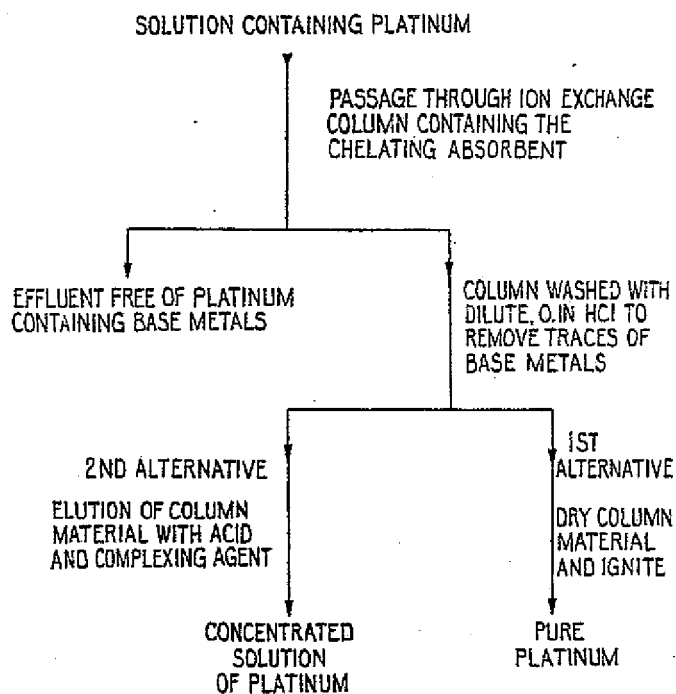
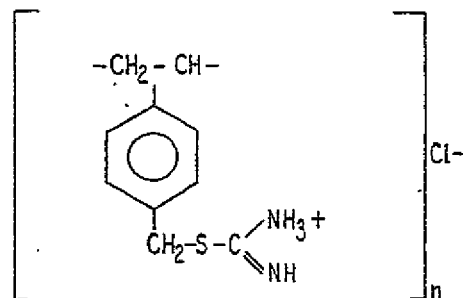
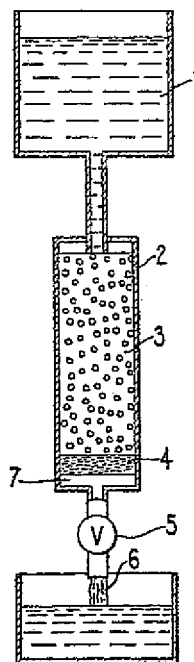


FIG.1

FIG.2FIG.3

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